# Composition gradient-enabled circular photogalvanic effect in inogranic halide perovskites ®

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#### ABSTRACT

Inversion symmetry breaking could lead to the creation of a Rashba–Dresselhauls magnetic field, which plays the key role in spintronic devices. In this work, we propose and develop a composition gradient engineering approach that breaks inversion symmetry into inorganic halide perovskites with strong spin–orbit coupling. We synthesize epitaxial CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> with Br/Cl composition gradient by a two-step chemical vapor deposition approach. Through optoelectronic measurements, we show the presence of circular photogalvanic effects (CPGEs), evidencing a Rashba-like spin polarized band structure. By spatially resolved photoluminescence spectra, we find that the observed CPGE is likely a cumulative result of inversion symmetry-broken interfaces featured by abrupt and stepwise composition gradient between the pristine and separated daughter phases. Our work suggests an avenue in engineering the spintronic property of halide perovskites for information processing.

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Spintronic devices are expected to deliver energy-efficient and high-speed computing.<sup>1–6</sup> An important aspect related to spintronics is spin–orbit coupling (SOC).<sup>7,8</sup> For solids, when inversion symmetry is broken, SOC gives rise to the Rashba–Dresselhaus effect by which the twofold spin degeneracy is lifted.<sup>9–12</sup> The Rashba–Dresselhaus field allows the control of spin precession.<sup>12,13</sup> The Rashba–Dresselhaus effect has been revealed in many materials systems such as heavy metals/semiconductors,<sup>14,15</sup> topological insulators,<sup>16–18</sup> Weyl semimetals,<sup>19–21</sup> two-dimensional (2D) crystals/heterostructures,<sup>22–24</sup> and hybrid organic–inorganic perovskites (HOIPs).<sup>25–29</sup>

3D halide perovskites are characterized by a general formula AMX<sub>3</sub>, where A is an organic group or inorganic cation such as  $Cs^+$  or  $MA^+$ , M is a heavy metal cation such as  $Pb^{2+}$  or  $Sn^{2+}$ , and X is a halide anion including Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>. AMX<sub>3</sub> are widely studied due to promising optoelectronic properties.<sup>30–35</sup> These properties together with heavy metal Pb carrying strong SOC in 3D halide perovskites make them excellent candidates for exploration of Rashba–Dresselhaus optospintronics.<sup>7,10</sup> So far, most studies of the Rashba–Dresselhaus effect in halide perovskites have been based on HOIPs with either the crystal structure lacking inversion symmetry or the device structure dominated by interfaces.<sup>7,10,28,36–48</sup> It has been under debate that whether the 3D organic–inorganic perovskite has intrinsic inversion symmetry or not.

This debate associated with the alignment of the organic molecules influences the elucidation of the source of the observed Rashba–Dresselhaus effect in some perovskite devices.<sup>7,49,50</sup>

In this work, we introduce inversion symmetry breaking in epitaxial inorganic 3D halide perovskites through the composition gradient. We design a Br/Cl composition gradient along the in-plane x direction of CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub>, as shown in Fig. 1(a). Here, a monotonic change in the concentration of Br/Cl is designed along the *x* direction [e.g., more Br atoms in the left and less on the right in Fig. 1(a)]. Figure 1(b) shows a part of the CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> lattice, where we can identify such a composition-modified structure with a point group  $C_{4\nu}$ (assuming a pseudocubic structure). It has a fourfold rotation symmetry with the rotation axis along the x axis and two mirror planes xy and xz. Figure 1(c) depicts the schematic band structure in momentum space for an inorganic perovskite, e.g., CsPbBr3 with inversion symmetry, where a linear s-like combination of Pb 6s- and Br 5porbitals forms the valence band maximum (VBM) [Fig. 1(d)], and the degenerated Pb 6p-orbitals [Fig. 1(e)] form the conduction band minimum (CBM). For CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> with inversion symmetry breaking</sub>(i.e., with a  $C_{4\nu}$  point group), Fig. 1(f) shows its band structure where Rashba-Dresselhaus band splitting is expected. Such a band structure is derived based on the density functional theory calculation of



**FIG. 1.** Theoretical design of the composition gradient-enabled spin-polarized band structure through Rashba–Dresselhaus effects. (a) Top view of the proposed structure of CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> with composition gradient of Br/Cl along the x direction. (b) CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> structure has a fourfold rotation axis (x axis) and two mirror planes (xy, xz). (c) Schematic band structure of CsPbBr<sub>3</sub> without composition gradient. (d) Linear combination of Pb 6s- and Br 5p-orbitals (s-like) with antibonding configuration for VBM. (e) One Pb 6p-orbital for CBM. (f) Schematic band structure with Rashba–Dresselhaus effects induced by the composition gradient.

CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> with prescribed symmetry breaking of the same point group.<sup>48</sup> In Fig. 1(f), the directional green and red arrows denote the spin-up  $(m_s = +\frac{1}{2})$  and spin-down  $(m_s = -\frac{1}{2})$  states, respectively.  $\sigma^+$ and  $\sigma^-$  represent right-circularly polarized (RCP) light (S = +1) and left-circularly polarized (LCP) light (S = -1), respectively. Since the VBM is formed by s-like orbitals whose orbital angular momentum is 0 (i.e., l = 0),  $m_i$  is equal to  $m_s$ . For the CBM, due to the dominance of p-orbitals contributions, l = 1. The optical selection rule for circularly polarized light would allow the absorption of  $\sigma^+$  photons between the CBM and VBM in the  $-k_y/-k_z$  valley (i.e., from  $m_s = -\frac{1}{2}$  to  $m_i = +\frac{1}{2}$ ), and the absorption of  $\sigma^-$  photons in the  $k_y/k_z$  valley (i.e., from  $m_s = +\frac{1}{2}$  to  $m_i = -\frac{1}{2}$ ). This spin-polarized band splitting can be revealed experimentally by circular photogalvanic effects (CPGEs), where photocurrents of opposite directions between RCP and LCP illuminations are expected. An optical orientation approach is also common in investigating other SOC-related phenomena<sup>51-55</sup> such as inverse spin-Hall effects.

Figure 2(a) illustrates a two-step chemical vapor deposition (CVD) process for our film growth. First, we deposited a CsPbCl<sub>3</sub> film on a freshly cleaved NaCl substrate horizontally aligned in the chamber at 600 °C. In this step, the thickness of CsPbCl<sub>3</sub> will reduce along the air flow direction (i. e., +x direction) due to the diffusion length limit.<sup>56</sup> Then we conducted a second deposition at 500 °C with precursors set for CsPbBr<sub>3</sub>. We set the sample with a 45°-oblique angle in the growth chamber for thickness uniformity. At the same time, a high temperature will enable the diffusion of Cl<sup>-</sup> and Br<sup>-</sup>. Details on the growth conditions are shown in supplementary note I. As a control experiment, a pure CsPbCl<sub>3</sub> epitaxial film was grown on NaCl without the second growth step. Figure 2(b) shows an x-ray diffraction (XRD) pattern of the CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub>/NaCl heterostructure and the NaCl

substrate. The crystal structure for  $CsPbBr_xCl_{(3-x)}$  could be assigned to the orthorhombic structure.  $^{57-59}$  Strong peaks at  $2\theta\,{=}\,15.2^\circ$  and  $30.6^{\circ}$  shown in the inset can be assigned to CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub>(002) and (004) (see details in supplementary material note II). Figure 2(c) shows the XRD patterns for CsPbCl<sub>3</sub>/NaCl and NaCl. The CsPbCl<sub>3</sub>(004) peak is close<sup>60</sup> to and overwhelmed by the NaCl(002) peak. The inset is an enlarged CsPbCl<sub>3</sub>(002) peak at 15.8° for comparison. It is worth noting that there are clear shoulders for both CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub>(002) and (004) peaks. As it will become clear later, the large full width at half maximum (FWHM) is consistent with the observation of a gradual change of the Br composition across the *x*-direction of the film by other means. The XRD patterns reveal the out-of-plane epitaxial relation:  $CsPbBr_xCl_{(3-x)}(001)||NaCl(001).$ The in-plane orientation of the epitaxial heterostructure is investigated by the x-ray azimuthal  $\varphi$  scan in Fig. 2(d). Here, for convenience, we index  $CsPbBr_xCl_{(3-x)}$  with a pseudocubic structure.<sup>57,61</sup> The (224) reflections of CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> and NaCl are at the same  $\varphi$ angle, indicating an in-plane epitaxial relationship for the heterostructure as  $CsPbBr_xCl_{(3-x)}[100]$  ||NaCl[100].

The composition gradient in CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> is further investigated by position-dependent photoluminescence (PL) spectra and energy-dispersive x-ray spectroscopy (EDS) analysis. The PL spectrum was collected at a spatial interval of 0.3 mm along the *x* direction and is normalized in Fig. 2(e). The wavelength at each peak is replotted in Fig. 2(f), which shows a clear red shift along the +*x* direction. Since PL peaks for pure CsPbBr<sub>3</sub> and CsPbCl<sub>3</sub> are located at 521<sup>57</sup> and 415 nm,<sup>62</sup> respectively, the observation suggests a gradual composition for Br/Cl. Figure 2(g) shows the Br/Pb ratios along the *x* direction extracted from EDS. The evidence of the composition change of Br in CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> should induce a wide range of lattice



**FIG. 2.** Structural and compositional characterizations. (a) A two-step CVD growth process. (b) XRD patterns of the CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> film and the NaCl substrate. (c) XRD patterns of the CsPbCl<sub>3</sub> film and the NaCl substrate. (d) X-ray  $\varphi$  scan of NaCl(224) and CsPbCl<sub>3</sub>(224) and NaCl(224) and CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> film. (e) Normalized PL spectra along the x direction of the CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> film. (f) Replot of PL peak wavelengths in (e). (g) Br/Pb ratios along the x direction of the CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> film. The inset shows a cross-sectional scanning electron microscopy (SEM) image. The red box is the area for collecting EDS.

constants along the *x* direction, which are consistent with the widened FWHM in Fig. 2(b).

To conduct CPGE measurement for confirming the spinpolarized band structure, the device is configured in a manner with the current direction being perpendicular to the rotation axis (*x* direction). Figure 3(a) shows the schematic drawing of the device where the device channel is along the *y* direction. The channel length is 60  $\mu$ m and can be homogenously covered by the laser beam. The laser propagates through a quarter-waveplate (QWP) to the channel, and the incident plane is perpendicular to the channel direction *y*. The laser incident angle  $\alpha$  is with reference to the *z* axis while  $\varphi$  is the angle between the fast axis of the QWP and the polarization direction of the incident beam. Thus the polarization of an incident beam can be modulated from linear polarization (LP) to RCP, to LP, then to LCP and finally back to LP, by rotating the QWP.

The CPGE current is commonly expressed by a phenomenological equation,<sup>63</sup> which consists of four contributions

$$I = C\sin 2\varphi + L_1\sin 4\varphi + L_2\cos 4\varphi + D, \tag{1}$$

where the helicity-dependent parameter *C* accounts for CPGE.  $L_1$  and  $L_2$  account for the linear photogalvanic effect (LPGE) or photon drag effect.<sup>24,64,65</sup> It should be noted that *C*,  $L_1$ , and  $L_2$  all depend on the incident angle,  $\alpha$ . *D* accounts for all the polarization-independent background current.<sup>24,66–68</sup> Further discussion on the LPGE term is provided in the supplementary material, Note III.

The CPGE-related parameter *C* in the CPGE term is related to a second-order tensor,  $\beta_{ij}^C$ . For crystals with the lowest symmetry  $C_1$ , the CPGE tensor  $\beta_{ij}^C$  can be represented as

$$\beta_{ij}^{C} = \begin{bmatrix} \beta_{11}^{C} & \beta_{12}^{C} & \beta_{13}^{C} \\ \beta_{21}^{C} & \beta_{22}^{C} & \beta_{23}^{C} \\ \beta_{31}^{C} & \beta_{32}^{C} & \beta_{33}^{C} \end{bmatrix}.$$
 (2)

Thus, the CPGE current,  $I_i^c$ , can be calculated as

$$\frac{I_i^C}{A} = i\beta_{ij}^C \Big( \boldsymbol{E}_{\boldsymbol{j}} \times \boldsymbol{E}_{\boldsymbol{j}}^* \Big), \tag{3}$$

where *A* is the electrode area, *i* is the unit imaginary number, *E* is the incident light polarization vector,  $\beta^{C}$  is the CPGE tensor, and subscripts *i* and *j* are index notations. When the *xz* plane is the laser incident plane and the short-circuit current is measured along the *y* direction, as is in our device configuration,

$$\frac{I_y^C}{A} = I_0 \sin 2\varphi \left(\beta_{21}^C \sin \alpha - \beta_{23}^C \cos \alpha\right),\tag{4}$$

where  $I_0 = |E|^2$  is the laser energy density on the channel.

Since the channel is along the y direction, from Eq. (1), we can also define the CPGE current as

$$I_{y}^{C} = C\sin 2\varphi. \tag{5}$$

Combining Eq. (5) with Eq. (4), we can get

$$C = AI_0 \left( \beta_{21}^C \sin \alpha - \beta_{23}^C \cos \alpha \right). \tag{6}$$

We first investigate the CPGE current,  $I_y$ , as a function of beam polarization at different incident angles,  $\alpha = 0^{\circ}$ ,  $30^{\circ}$ , and  $45^{\circ}$  [Fig. 3(b)]. The experimental data are fitted using Eq. (1) with solid lines, from which we can obtain all four parameters, *C*,  $L_1$ ,  $L_2$ , and *D*. For



**FIG. 3.** CPGE measurement for the CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> device. (a) Experimental setup. The inset shows a photo of the real device. (b) Polarization-dependent photocurrent at different incident angles,  $\alpha$ . Dashed lines are the measured data, and solid lines are the fitting curves. For clarity, polarization-independent photocurrents, *D*, are subtracted, and a constant offset is added. (c) CPGE-related term, *C*, as a function of the incident angle,  $\alpha$ , extracted from fitting curves. (d) Polarization-dependent photocurrent at different laser energy densities at  $\alpha = 30^{\circ}$  and  $-30^{\circ}$ . Dashed lines are the measured data, and solid lines are the fitting curves. (e) CPGE-related term, *C*, as a function of the laser energy density, extracted from the fitting curves in (d).

clarity, the polarization-independent background photocurrent, *D* is subtracted. Figure 3(c) shows the CPGE-related parameter *C* as a function of  $\alpha$  extracted from the fitting curves. All parameters *C*,  $L_1$ ,  $L_2$ , and *D* are summarized in the supplementary material, Note III. We can also obtain the tensor elements,  $\beta_{23}^{C} \approx -7.97 \times 10^{-4} \text{ V}^{-1}$  and  $\beta_{21}^{C} \approx 9.86 \times 10^{-5} \text{ V}^{-1}$  from Eq. (6). The absolute value of  $\beta_{23}^{C}$  is almost one order in magnitude larger than  $\beta_{21}^{C}$ , indicating that the composition gradient along *x* plays a major role in inducing the CPGE current. The inhomogeneous electric field near the electrode area along the *z* direction can also break the local symmetry and contribute to small  $\beta_{21}^{C}$ , which is illustrated in the supplementary material, Note VII.

Figure 3(d) shows the CPGE current as a function of the beam polarization with different laser energy densities at  $\alpha = -30^{\circ}$  and  $30^{\circ}$ . CPGE-related parameter *C* as a function of the laser energy density is replotted in Fig. 3(e). The result follows the relationship in Eq. (6),  $C \propto I_0$ . Moreover, according to Eq. (6) and the tensor elements extracted from Fig. 3(c), *C* is calculated to be 61.2 pA for  $\alpha = -30^{\circ}$  with a laser energy density of 0.53 mW/cm<sup>2</sup>. The measured *C* at  $-30^{\circ}$  is 65.4 pA, consistent with the result calculated in Eq. (6). Measurement results at both  $\alpha = -30^{\circ}$  and  $30^{\circ}$  are aligned with the proposed symmetry in our device.

However, the observed composition gradient is too small to enable measurable CPGE at room temperature. To understand the underlying mechanism leading to the observed CPGE, we have conducted further spatially resolved PL measurements. Recent studies illustrate the phenomenon and theoretical analysis of the spinodal decomposition in mixed halide perovskites.<sup>69,70</sup> The uniform mixture can be deposited at elevated temperatures. However, when we lower down the temperature, the pristine phase becomes unstable due to the reduction of entropy contribution. For *TS* term in G = H - TS, see details in the supplementary material, Note V. Here, T is temperature, S entropy, G Gibbs free energy, and H enthalpy. The pristine perovskite  $CsPbBr_xCl_{(3-x)}$ , thus, will decompose to  $Br^{++}$  and  $Cl^{++}$  phases. It is a slow process at room temperature, which can be accelerated by high power light illumination.<sup>71,72</sup> Our CPGE measurement is conducted eight days after deposition while the characterizations in Fig. 2 were carried on freshly prepared samples. After storing for eight days at room temperature under indoor light, we collected PL spectra with a spatial interval of 0.1  $\mu$ m along the x direction. Figure 4(a) shows one set of PL spectra within a 40 µm-long local area. For better visualization, we show a spectrum every  $1 \,\mu m$  along the x direction, and there are 40 spectra for the 40- $\mu$ m distance along the x direction. All 27 figure panels for the 1.08 mm film are shown in supplementary note V. Different from the PL spectra for the freshly deposited film, another peak at  $\sim$ 507 nm appears besides the peak for the CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> pristine phase. As widely reported in the literature,<sup>71,73,74</sup> the new peak comes from a new phase, which is a consequence of phase separation of the unstable pristine phase. We name this new phase as the Br<sup>+</sup> phase. According to the phase diagram, when there is the Br<sup>++</sup> phase, there will be the Cl<sup>++</sup> phase due to mass conservation (see details in the supplementary material, Note V). However, in our experimental setup, an optical filter is inserted to block the light shorter than 420 nm to protect the CCD from damaging by the source laser (405 nm). The amount of the Cl++ phase can be estimated by the lever rule. The PL peak intensity ratios of Br++ to the pristine phase are extracted and replotted in Fig. 4(b), which can reflect the molar ratio of  $Br^{++}$  to the pristine phase. Based on this observation, the schematic of a possible phase distribution for this 40- $\mu$ m area is shown in Fig. 4(c). The steep decrease in the intensity ratio at  $\sim$ 30  $\mu$ m in Fig. 4(b) indicates the existence of an interface between the new phases and the pristine phase,



**FIG. 4.** Interfaces induced by phase separation in pristine halide perovskite  $CsPbBr_xCl_{(3-x)}$ . (a) A set of consecutive PL spectra collected from a 40  $\mu$ m-long area along the *x* direction. (b) PL peak intensity ratio of the Br<sup>++</sup> phase over the pristine phase in (a) for all consecutive 400 spectra (one spectrum per 0.1  $\mu$ m). (c) Schematic phase distribution for the 40- $\mu$ m long area in (a) and (b). (d) PL peak intensity ratio of the Br<sup>++</sup> phase over the pristine phase along the *x* direction in 1.08 mm. (e) Schematic phase distribution in the CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> film over 1.08 mm. Interfaces between Br<sup>++</sup> and pristine and Cl<sup>++</sup> and pristine phases are highlighted with dashed boxes. (f) and (g) Schematic conduction band structure at the interface between Br<sup>++</sup> and pristine phases and Cl<sup>++</sup> and pristine phases, respectively. (h) and (i) Schematic spin texture near the conduction band minimum at the interface between Br<sup>++</sup> and pristine phases and Cl<sup>++</sup> and pristine phases, respectively.

which is highlighted by black boxes in Fig. 4(c). Figure 4(d) shows the PL intensity ratio along the *x* direction for the 1.08 mm CsPbBr<sub>x</sub>Cl<sub>(3-x)</sub> film. Every data point is the averaged result over 400 PL spectra collected for a 40  $\mu$ m long area along the *x* direction. In this 8-day-old sample, the PL peak intensity ratio fluctuates locally but macroscopically decreases along the *x* direction, suggesting the relevant molar ratio of the Br<sup>++</sup> over the pristine phase. This observation suggests that less phase separation occurs in the region where the pristine phase has more Br. This is reasonable since for the pristine sample with high molar ratio of Br, the driving force for phase separation is low<sup>75</sup> (see details in the supplementary material, Note V). The macroscopic decreasing trend of phase separation can be schematically described in Fig. 4(e). There will be interfaces between separated phases and the pristine phase, which can be confirmed also in Figs. 4(b) and 4(c). Such an interface can be extremely sharp.<sup>76</sup>

We assign the interface between the pristine phase and the Cl<sup>++</sup> phase as Interface<sub>Cl</sub> and the one between the pristine phase and the Br<sup>++</sup> phase as Interface<sub>Br</sub>. There will be inversion symmetry breaking at these interfaces since the composition difference exists. Both interfaces lead to the generation of a  $C_{4\nu}$  point group locally. However, the direction of local electric fields at Interface<sub>Cl</sub> and Interface<sub>Br</sub> is opposite because of the opposite composition difference at two interfaces. This will induce the different band splitting schematically shown in Figs. 4(f) and 4(g). Spin-up and spin-down bands will split oppositely along the  $k_{\gamma}$  and  $k_{z}$  directions. At the same temperature and illumination condition, the current generated at these two interfaces will flow to the opposite direction. The splitting energy  $E_R$  will also be different (see details in the supplementary material, Note V). Figures 4(h) and 4(i) show the schematic spin-texture near the conduction band minimum

for the Br<sup>++</sup>/pristine interface and the Cl<sup>++</sup>/pristine interface, respectively, which also reveals the opposite spin direction both in inner and outer bands and the different  $E_R$ . According to our experimental observation, the net current due to the cumulative contributions of  $I_{\text{Interface}_G}$ and  $I_{\text{Interface}_R}$  is not zero (see details in the supplementary material, Note V). In addition, if there is no composition gradient along the *x* direction, there will be no macroscopical decreasing trend of the phase separation (see details in the supplementary material, Note V).

As a control experiment, a  $60 \,\mu$ m-channel device on pure CsPbCl<sub>3</sub> was prepared. The device also has a configuration as shown in Fig. 3(a). Our test shows that without composition gradient there is no CPGE (see the supplementary material, Note VI).

In summary, by a two-step CVD growth process, we achieved the composition gradient in  $CsPbBr_xCl_{(3-x)}$ . The CPGE is proposed to be a cumulative result of the inversion symmetry-broken interfaces induced by phase separation. This work suggests an approach in designing halide perovskites materials for spintronic applications.

See the supplementary material for notes I–VII: experimental method, LPGE, and CPGE fitting results.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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